Test bench for electricity or hydrogen production from aqueous methanol

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Abstract:
The growing demand for renewable energy sources, sometimes far from the place of consumption, has led to consider the conversion of these energies into fuels, allowing its transport and storage. This is the case of hydrogen, which can be transported in form of methanol, more suitable for transport and storage, obtained by the synthesis process of CO_2 and hydrogen. In this way, the application of methanol as an energy vector arises. Once methanol reaches its place of use, it can be used as a fuel in Direct Methanol Fuel Cells (DMFC) or transformed back into hydrogen using methanol electrolysis. However, there are at present several challenges to be forced. While DMFC present several still unsolved issues such as poor methanol oxidation reaction, fuel crossover or high demand of noble metal, methanol electrolysers have operational limits produced by problems related to active site blockage by the formation of adsorbed carbonaceous species, sluggish kinetics, or methanol crossover.
For the study of DMFC and methanol electrolysers and implement improvements in their design, a test bench that allows testing both devices independently has been designed and built. It allows plotting polarization curves, analysing crossover and developing electrochemical impedance spectroscopy studies, as well as the control of operating temperature of the devices, the mass flow, pressure and temperature of the oxygen or nitrogen introduced in the DMFC and methanol flow rate. These features will become key factors for the development of technologies for improving the use of methanol as an energy vector.

Keywords:
Methanol electrolysis; hydrogen production; test bench; electricity production; DMFC; methanol

1. Introduction

Renewable energy sources are those obtained from inexhaustible natural resources, such as the sun or wind. These energy sources have the advantage of being cleaner and more sustainable than fossil fuels. However, renewable energies also present some challenges, such as their intermittency. Energy that is not consumed during peak energy production from renewable sources can be stored in chemical form and used when needed. One of the fuels that can be generated using electricity is hydrogen [1]. This is the most abundant element in the universe and can be used to generate electricity or power vehicles [2]. Hydrogen has a high specific energy and its consumption in fuel cells produces only water, making it a very attractive option for reducing greenhouse gas emissions [3]. Green hydrogen, which is produced from renewable energies sources, is environmentally friendly, but also expensive and not easy to store and transport [4].

Methanol is an alcohol that can be used as an alternative fuel for internal combustion engines or fuel cells [5]. This fuel can be produced from a variety of sources, such as hydrogen and carbon dioxide [6]. Methanol has the advantage that it takes up less volume than hydrogen and can be more easily transported and stored because methanol is a liquid chemical compound at ambient temperature and pressure. In addition, methanol can be produced using electricity from wind or solar power to generate hydrogen and then combining it with carbon dioxide captured from the atmosphere or industrial sources [7]. This fuel is known as e-methanol and produces a carbon-neutral fuel that contributes to the decarbonisation of the economy [6].

Methanol can be used to generate electricity or hydrogen. Direct methanol fuel cells (DMFC) are devices that use methanol as fuel and produce electricity, water and carbon dioxide [8]. However, they also present some challenges, such as low efficiency, high methanol permeation loss through the membrane, low CO tolerance and degradation of components [8-9]. DMFC fuel cells are fed with methanol and oxygen to produce direct current electricity. Methanol in aqueous solution is fed to the anode and oxygen is fed to the cathode. The reactions that occur during the operation of a DMFC single cell are shown in Eqs. (R1-R2). Equation (R1)

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represents the half-reaction at the anode, Eq. (R2) represents the half-reaction at the cathode and Eq. (R3) represents the overall reaction [10].

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (R1)

Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (R2)

Overall: $CH_3OH + \frac{3}{2}O_2 \rightarrow 2H_2O + CO_2$ (R3)

Methanol electrolysers are devices that use electricity to produce hydrogen from aqueous methanol. They have the advantage that the hydrogen produced is of high purity. However, they also present some challenges, such as low efficiency [11-12]. Methanol is introduced at the anode, while no reactant is introduced at the cathode. In Eqs. (R4-R6) are presented the half-reactions taking place at the anode, cathode and the overall reaction, respectively [11-12].

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (R4)

Cathode: $6H^+ + 6e^- \rightarrow 3H_2$ (R5)

Overall: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ (R6)

Several lines of research are underway to improve the performance of DMFC and methanol electrolysers. For example, the development of new membranes with lower permeability to methanol, higher ionic conductivity and higher chemical and mechanical stability [13]. Also, the development of new catalysts with higher activity and selectivity for methanol oxidation and oxygen reduction is undertaken [14]. In addition, the channel configuration of the bipolar plates can be studied to increase the power density of DMFC or to decrease the voltage required for a methanol electrolyser [9,15]. In order to study how these modifications affect the performance of both devices, a test bench is needed.

This work presents the design and operation of a test bench for a DMFC and methanol electrolyser. In the first section, the configuration of the test bench is presented. The second section presents the results obtained for DMFC and methanol electrolyser. Finally, the conclusions are exposed.

2. Configuration of the DMFC and methanol electrolyser test bench

There are several tests that can be conducted to study the performance of DMFC and methanol electrolysers, and the configuration of the test bench depends on these tests. This section presents some of the tests that can be performed and the characteristics of the test bench designed in this work.

2.1. Tests to be performed with the test bench

The aim of this work is to design and build a test bench to investigate the performance of a DMFC and a methanol electrolyser under different operating conditions. To determine this performance, various tests can be carried out for both devices, including polarization curve tracing, crossover tests and electrochemical impedance measurements [16].

A polarization curve test is used to determine the operation and performance of a fuel cell or an electrolyser. With this measurement, the relationship between the voltage and current generated or applied to the cell can be obtained, as well as the voltage losses due to different types of factors. To do this test a DMFC single cell in this work the evolution of the current density generated by the cell is measured as the voltage decreases. To test a methanol electrolyser single cell with this bench the voltage is measured as the current density increases.

A crossover test is used to measure the amount of fuel diffusing through the membrane from the anode to the cathode without being oxidised at the anode. This measurement can provide information on the efficiency and durability of the cell. The test performed consists of feeding the anode with the fuel and the cathode with an inert gas (e.g., nitrogen) and measure the current generated by the reaction of the fuel present in the cathode.

An electrochemical impedance spectroscopy (EIS) test is used to characterise the electrochemical behaviour of a fuel cell. This measurement can provide information on the internal resistance, reaction kinetics and mass transport processes occurring in the fuel cell. The test consists of applying a small sinusoidal current to the cell and measure the frequency response of the system.

All these tests are performed by setting the values of oxygen or nitrogen mass flow rate and pressure, methanol mass flow rate and the temperature at which the device is operating.

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2.2. Experimental test bench

Depending on the type of test to be performed and the device under study, the test bench has different configurations. Figure 1 shows the diagram of the test bench for the DMFC study. In this diagram, a dashed line for the supply and treatment of oxygen or nitrogen can be seen. There is a cylinder for each gas used (1) to which a pressure regulator (2) is connected to control the pressure of the gas to be introduced into the system. A flow controller (3) is located downstream of this valve, which allows the flow rate of the gas introduced during the tests to be set. Before being introduced into the DMFC, the oxygen or nitrogen passes through a humidification system (4) so that the DMFC membrane is always wet during the tests (13). This system consists of two scrubber flasks arranged inside a thermostatic bath. After leaving the DMFC, the gas passes through a water trap (5) to prevent liquid water produced during the reaction from reaching the pressure controller (6), which controls the operating pressure of the DMFC. Fuel is supplied to the DMFC from an aqueous methanol tank (7) using a pump (8).

To control the temperature at which the tests are carried out, there are two chambers (9). The device to be tested is placed in the inner chamber and kept at the desired temperature. To achieve this effect, there is a refrigerated and heating circulator (10) which circulates distilled water to a heat exchanger (11) at the temperature required to increase or decrease the temperature inside the chamber. To force the recirculation of air between the two chambers, a fan is connected to the heat exchanger and powered by a power source (12).

Finally, a potentiostat-galvanostat (14) connected to a computer (15) is used to control the voltage values at which the DMFC operates, while the current and impedance parameters are recorded during the tests for subsequent analysis.

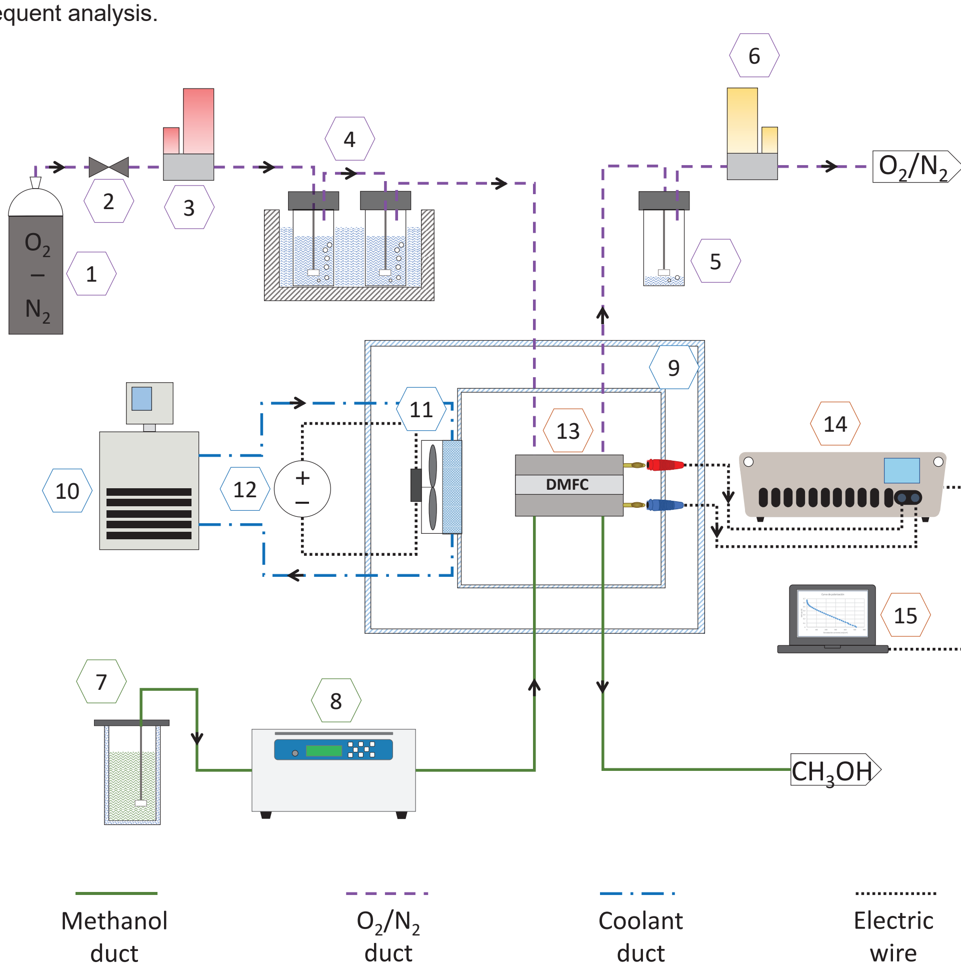

Figure 1. Diagram of the test bench when it is used to test Direct Methanol Fuel Cells. 1 - Compressed O_2/N_2 cylinder. 2 - Pressure reduction valve. 3 - Gas flow controller. 4 - Gas humidification system. 5 - Water trap. 6 - Gas pressure controller. 7 - Aqueous methanol tank. 8 - Methanol pump. 9 - Chamber. 10 - Refrigerated and heating circulator. 11 - Heat exchanger. 12 - Power source. 13 - DMFC. 14 - Potentiostat-galvanostat. 15 - Computer.

3. Results and Discussion

After the assembly and set-up of the test bench presented in Fig. 2, it has been possible to obtain polarization curves of a DMFC single cell and for a methanol electrolyser single cell. The single cells of both devices consist of 316L steel plates with serpentine channels, with an active area of 16 cm^2. The MEA used for each device consists of a Nafion® 117 membrane and commercial electrodes corresponding to the cathode and anode. The cathode uses Freudenberg carbon paper as support with a Pt 1mg/cm^2 catalyst load. For the anode, the same support is used, but with a Pt-Ru charge of 3 mg/cm^2.

Figure 2. The test bench designed and built to study DMFC and methanol electrolysers.

3.1. DMFC polarization curves

Figure 3 shows the polarization and power density curves obtained for the DMFC with the test bench at different oxygen mass flow rates to study the effect of this parameter on the DMFC performance. All curves have been obtained at a temperature of 60 °C, 1 bar pressure and a methanol concentration of 1 M and flow rate of 3 ml/min.

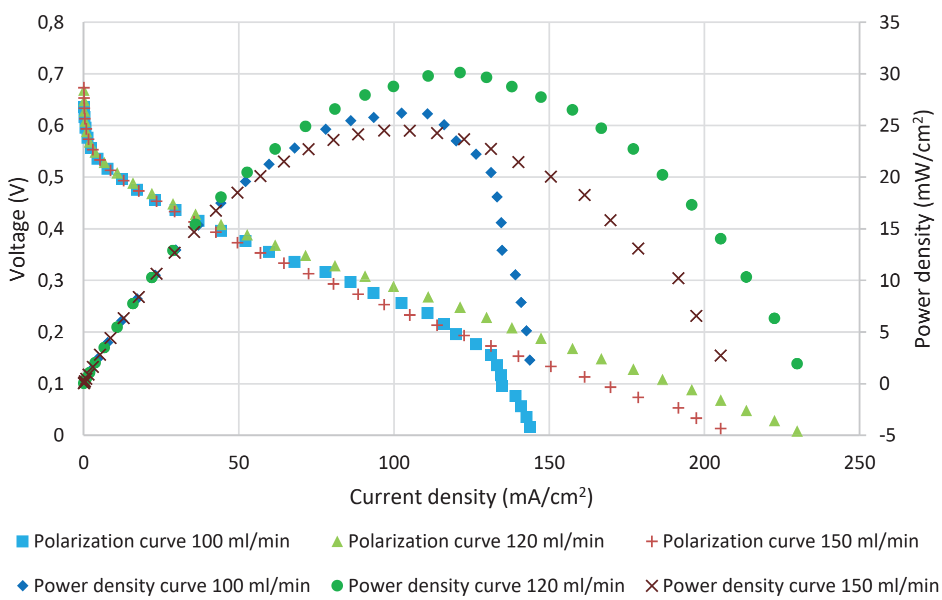

Figure 3. Polarization and power density curves of the DMFC single cell for different oxygen flow rates obtained at a temperature of 60 °C, pressure of 1 bar and a methanol concentration of 1 M and flow rate of 3 ml/min.

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It can be seen from Fig. 3 that for a volumetric oxygen flow rate of 110 ml/min the current density increases slightly as the voltage values decrease below 0.23 V, with the current density not following the trend shown up to this voltage value. This results in a large decrease of the power density after having reached the maximum value. This behaviour of the single cell for this volumetric flow of oxygen can be attributed to that this flow is not able to extract from the cathode channels the water that has been generated during the polarization curve, thus blocking the reaction at the last points of the curve. To avoid this, the oxygen flow rate is increased, with best results at 120 ml/min. However, when increasing the flow rate to 150 ml/min, the Nafion® membrane probably starts to dry out during the polarization curve and for this reason the peak power density value is lower.

3.2. Methanol electrolyser polarization curves

Figure 4 shows the polarization curves of the methanol electrolyser obtained with the test bench at different temperatures to evaluate the effect of this parameter in the performance of the electrolyser. The concentration of methanol used to feed the electrolyser is 1 M and the aqueous methanol flow rate is 6 ml/min.

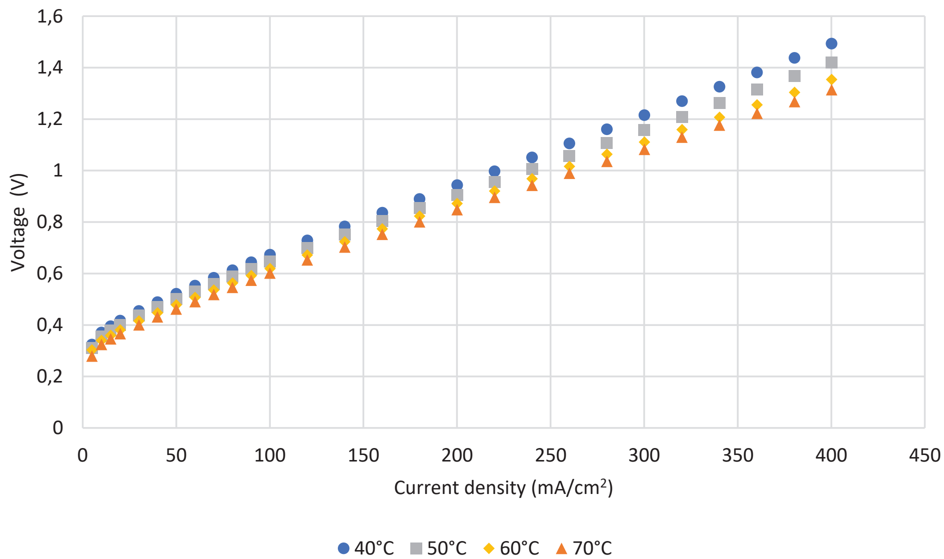

Figure 4. Polarization curves of the methanol electrolyser single cell for temperatures of 40 °C, 50 °C, 60 °C and 70 °C obtained with aqueous methanol of concentration 1 M and methanol flow rate of 6 ml/min.

In Fig. 4 can be observed that while increasing temperature, the voltage decreases for the same current density. This results in a lower electrical energy consumption to produce the same mass of hydrogen with the methanol electrolyser when increasing temperature.

4. Conclusions

This article describes the design and assembly of a test bench to analyse the behaviour of DMFC and methanol electrolysers. The bench makes it possible to control the pressure and flow of oxygen or nitrogen, the flow of methanol in aqueous solution and the temperature at which the tests are carried out.

By performing polarization curves, crossover and EIS measurements with this test bench, the effects of each of the DMFC and electrolyser components, such as membranes, catalysts, electrodes or the flow path of the bipolar plates, on these devices can be evaluated.

From the results obtained so far it can be seen that the choice of the oxygen flow rate is an important parameter for a DMFC, as too little flow rate may indicate that the cathode channels become waterlogged and too much flow rate may indicate that the membrane dries out and blocks the reactions from taking place. It has also been shown that an increase in temperature in the case of the methanol electrolyser implies a decrease in energy consumption to continue producing the same amount of hydrogen with this device.

The test bench presented in this work allows to obtain very useful experimental results to study the influence of different parameters and components, both at experimental and commercial level, on the performance of a DMFC and a methanol electrolyser, allowing to further improve the technology of these devices.

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